

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08F 8/44	A1	(11) International Publication Number: WO 00/50473 (43) International Publication Date: 31 August 2000 (31.08.00)
(21) International Application Number: PCT/US00/04754 (22) International Filing Date: 25 February 2000 (25.02.00) (30) Priority Data: 11/48872 25 February 1999 (25.02.99) JP (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): NAKATA, Kazuyuki [JP/JP]; 2-4-1, Yushudai-nishi, Ichihara-shi, Chiba-ken (JP). (74) Agent: EVANS, Craig, H.; E.I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: AQUEOUS DISPERSION COMPOSITION AND MANUFACTURING METHOD FOR THE COMPOSITION (57) Abstract A uniform aqueous dispersion of ethylene-methacrylic acid copolymer having a good shelf-life obtained by using an excess amount of ammonia as a disperser.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5

TITLE**AQUEOUS DISPERSION COMPOSITION AND MANUFACTURING
METHOD FOR THE COMPOSITION****FIELD OF THE INVENTION**

The present invention relates to an aqueous dispersion
10 composition having good stability and dispersion properties and a process for
making it by dispersing an ethylene-methacrylic acid copolymer in water using
an amount of ammonia in excess of amount that would be needed to neutralize
methacrylic acid. It also relates to the application of this aqueous dispersion in
making coated substrates.

BACKGROUND OF THE INVENTION

Aqueous dispersion compositions of ethylene α,β -ethylenically
unsaturated carboxylic acid copolymers such as ethylene-acrylic acid copolymer
or ethylene-methacrylic acid copolymer are known and sold commercially. They
can be easily made by dispersing the readily available ethylene acid copolymers
20 in water using an alkali metal compound and are useful in various applications
such as coating film. However, because the film coated with such dispersion
compositions has a poor waterproofness, it cannot be used for applications
requiring a film that is waterproof.

It is known that an ethylene-acrylic acid copolymer can be used as
25 an excellent raw material for an aqueous dispersion composition obtained using
ammonia as dispersion aide. Although it has been difficult to obtain an aqueous
dispersion composition using ammonia alone, a film coated with such aqueous
dispersion should have a good waterproofness since there is no alkali ion to
absorb water.

30 Uniformly dispersing ethylene-methacrylic acid copolymer in
water using a mixture of ammonia and an alkali metal has been known to be
difficult. Such aqueous dispersions of ethylene-methacrylic acid copolymer
could be obtained by adding small amounts of a surfactant as a supplemental
disperser. However, because the coated film using such dispersions have both
35 poor waterproofness and bleed-out, causing contamination, it was not preferred.

An object of this invention is to find a way to use ammonia alone
as a dispersion aide to make a uniform aqueous dispersion composition of an
ethylene-methacrylic acid copolymer that is stable for a long time, that is has a
good shelf-life of say a year or more. Another object was to find a way to make a
40 film (or other substrate) that when coated with such an aqueous dispersion would
have good waterproofness.

5 SUMMARY OF THE INVENTION

Attempts to obtain such an aqueous dispersion of ethylene-methacrylic acid copolymer using ammonia in an amount equivalent to that of the carboxyl groups contained in an ethylene-methacrylic acid copolymer were unsuccessful in making uniform dispersions.

10 With continued research, it was found that a stable, uniform aqueous dispersion of ethylene-methacrylic acid copolymer could be obtained using an ethylene-methacrylic acid copolymer containing specific amounts of acid, and using ammonia in an amount greater than the amount of the carboxyl groups in the copolymer. It was also found that coating a film (or other substrate)
15 with such an aqueous dispersion could make a waterproof, coated film (or other substrate).

The present invention, claiming priority to Japanese Patent Application No. Hei 11[1999]-48872 which is incorporated herein by reference, relates to a process for making a uniform aqueous dispersion of ethylene-methacrylic acid copolymer having good dispersion stability and to the aqueous
20 dispersion made from such process. It also relates to a coated substrate such as a film that, when coated with the aqueous dispersion of the present invention, has good waterproof properties. It also relates to a laminate obtained by applying the above-mentioned aqueous dispersion composition on a substrate for coating and
25 drying to form a coated substrate.

The stable, uniform aqueous dispersion of the present invention consists essentially of a dispersion of component (A), an ethylene-methacrylic acid copolymer containing 15-35 wt% of methacrylic acid, and component (B), ammonia in an amount required for neutralizing 110-150% of the carboxyl
30 groups of component (A) in water. The ethylene-methacrylic acid copolymer preferably comprises 5-50 wt% of the dispersion and preferably has a melt flow rate of 50-2000 grams/10 minutes at 190°C/2160 gram load. Surfactants and the like are not needed and preferably are not used.

DETAILED DESCRIPTION OF THE INVENTION

35 “Consisting essentially of” means that the recited components are essential, while smaller amounts of other components may be present to the extent that they do not detract from the operability of the present invention.

“Copolymer” means polymers containing two or more monomers.

A stable, uniform ethylene acid-containing copolymer aqueous
40 dispersion composition can be obtained by mixing selected ethylene methacrylic acid copolymer in water in the presence of an excess amount of ammonia.

5 The ethylene acid-containing copolymer aqueous dispersion of the present invention consists essentially of a dispersion of component (A), an ethylene-methacrylic acid copolymer containing 15-35 wt% of methacrylic acid as the ethylene acid-containing copolymer, in water in the presence of component (B), ammonia used as a basic component in an amount greater than the amount of
10 the carboxyl groups of component (A).

Both good dispersion property and good dispersion stability can be obtained by using an excess of component (B) ammonia, particularly an amount sufficient for neutralizing 110-150% of the carboxyl groups of the above-mentioned acid-containing copolymer (A). The resulting aqueous dispersion can
15 be coated onto a substrate, such as a film, to make a coated substrate, particularly a coated film, that is not susceptible to moisture accumulation and has a good waterproofness.

It is suitable for ethylene-methacrylic acid copolymer (A) to contain 15-35 wt% or alternatively 15-25 wt%, particularly 18-30 wt%, of an
20 unsaturated carboxylic acid. In the case of using a copolymer containing an unsaturated carboxylic acid in an amount that is less than the above-mentioned range, it is difficult to obtain a composition having a good aqueous dispersion property. In the case of using a copolymer containing an unsaturated carboxylic acid in an amount that is more than the above-mentioned range, a stable
25 dispersion composition cannot be obtained and both the waterproofness and mechanical strength of the coated film are reduced.

An ethylene-methacrylic acid copolymer having a melt flow rate of 50-2000 grams/10 minutes, particularly 60-1500, at 190°C/2160 gram load is suitable. In the case of using a methacrylic acid copolymer having an extremely
30 low melt flow rate, an aqueous dispersion composition having a good dispersion property cannot be obtained. When using a copolymer having an excessively high melt flow rate, the coated film has a poor strength.

Besides ethylene and methacrylic acid, the copolymer may be copolymerized with other monomers including an unsaturated carboxylic acid
35 ester such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, isobutyl methacrylate, dimethyl maleate, or diethyl maleate; a vinyl ester such as vinyl acetate or vinyl propionate; and carbon monoxide, in an amount of 20 wt% or less, particularly 10 wt% or less.

The aqueous dispersion composition of the present invention
40 contains ammonia, which can neutralize an excess, particularly 110-150%, more particularly 120-140% of the carboxyl groups of copolymer (A), along with copolymer (A).

5 In the case of an aqueous dispersion composition of the present invention containing a lower amount of ammonia than the above-mentioned range, a stable aqueous dispersion composition cannot be obtained. In the case of an aqueous dispersion composition of the present invention containing a higher amount of ammonia than the above-mentioned range, gelling easily occurs.

10 The aqueous dispersion composition suitably has the copolymer (A) present in an amount of 5-50 wt%, preferably 5-30 wt%, and particularly 10-30 wt%.

15 The aqueous dispersion composition is obtained by introducing both ethylene-methacrylic acid copolymer (A) and ammonia (B) with water into a vessel, then stirring them at about 90 to about 150°C for a sufficient time to uniformly disperse the ethylene-methacrylic acid copolymer (A), preferably about 10 minutes to about 2 hours.

20 The aqueous dispersion composition has good stability and good shelf life, such that neither the particle size nor the viscosity is significantly changed over times of up to a year or more.

Additives

A variety of additives can be added to the aqueous dispersion composition if desired.

25 Examples of additives include polyalcohols such as glycerin, ethylene glycol, polyethylene glycol, and polypropylene glycol; lower alcohols such as water-soluble epoxy compounds, methanol, ethanol, n-propanol, or isopropanol; ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol diethyl ether, diethylene glycol monoethyl ether, and dipropylene glycol monomethyl ether; esters such as propylene glycol monoacetate and ethylene glycol monoacetate; antioxidants; weather resistant stabilizers; ultraviolet-ray absorbents; antistatic agents; pigments; dyestuffs; antibacterial agents; lubricants; inorganic fillers; blocking preventing agents; and adhesives.

Other Polymer Aqueous Dispersion Compositions

35 The aqueous dispersion composition of the present invention may be mixed with other polymer aqueous dispersion compositions ("Other Dispersions") with a weight ratio based on the solid components in the dispersions of about 10/90 to about 90/10, particularly 20/80-80/20.

40 The Other Dispersion(s) with which the aqueous dispersion composition of the present invention may effectively be mixed should have a pH of 7 or more. If the pH of the Other Dispersion(s) is less than 7, it should be

5 adjusted with ammonia to obtain a pH of 7 or more before mixing. Also, the
Other Dispersion should be one that is not gelled when it is mixed with the
aqueous dispersion composition of the present invention. It is suitable to choose
Other Dispersion(s) having an average particle size of 1-10000, preferably 1-
1000, particularly 5-500 nanometers (nm), and having a solid component amount
10 of 2-60 wt%, particularly 5-50 wt% of the dispersion. Preferably the particle size
of the Other Dispersion(s) should be substantially the same as the dispersion of
the present invention.

Examples of the Other Dispersion(s) include aqueous dispersions
of ethylene-acrylic acid copolymer (particularly those made using ammonia alone
15 as dispersing agent), polyvinyl acetate, ethylene-vinyl acetate copolymer,
polyvinyl chloride, polyvinylidene chloride, water-soluble acryl resins,
acrylamide resins, methacrylamide resins, acrylonitrile resins, styrene-acrylic
acid copolymer, water-soluble polyurethane resins, water-soluble styrene-maleic
acid copolymers, water-soluble polyurethane resins, styrene-butadiene
20 copolymers, high-impact polystyrene resins, butadiene resins, polyester resins,
acrylonitrile-butadiene copolymers, polyethylene resins, polyethylene oxide
resins, polypropylene-ethylene copolymers, maleic anhydride graft-
polypropylene-ethylene copolymers, polyethylene chloride, polypropylene
chloride, EPDM (ethylene-propylene-diene polymer), polypropylene chloride,
25 phenol resins, silicone resins, and epoxy resins. One or more types of these may
be used.

A mixed aqueous dispersion composition can be obtained by
stirring and mixing the two or more dispersion compositions at standard
temperature. The base resin of the dispersion composition of the present
30 invention may be melt-blended or dry-blended beforehand with the base resin of
the other dispersion composition to be mixed with it, followed by dispersion in
water. The present invention is not specifically restricted by any manufacturing
method.

Coatings on Substrates

35 The aqueous dispersion composition of the present invention or
mixed aqueous dispersion composition (aqueous dispersion composition of the
present invention with Other Dispersion(s)) can be applied on any type of
substrate as a coating. The coated substrate, particularly a coated film, made by
this method has a good waterproofness.

40 The aqueous dispersions can be applied to a substrate for coating
using a conventional method such as that using a roll coater or a bar coater, a
method involving spraying, a method using an air-knife coater, a method using a

- 5 brush, or a method involving a substrate in the aqueous dispersion. Water is evaporated and a uniform film can be obtained by heating and drying after coating.

Examples of the substrate include molded products made by molding an olefin copolymer such as high, medium, or low-density polyethylene, ethylene- α -olefin copolymer, ethylene-vinyl acetate copolymer, ethylene-
 10 (meth)acrylic ester copolymer, ethylene-(meth)acrylic acid copolymer or ionomer, ethylene-(meth)acrylic acid-(meth)acrylic ester copolymer or ionomer, polypropylene, poly-1-butene, or poly-4-methyl-1-pentene; styrene resins such as polystyrene, ABS resin, or styrene-butadiene block copolymer; polyesters such as
 15 polyethylene terephthalate; polyamides such as nylon 6 or nylon 66; polyvinyl chloride; or their blends; natural materials such as a film, metal (iron, copper, aluminum, or stainless steel), wood, or paper; natural or synthetic leather; fibers such as nylon, polyester, acryl, urethane, or rayon; and fabrics.

The thickness of the coated film is not specifically restricted, but is suitably 1-20 micrometers (μm), particularly 1-5 μm . The coated film may be crosslinked by irradiating using an electron beam to improve the waterproofness or durability.

EXAMPLES

The following examples are illustrative of the present invention.
 25 All parts in the following examples are based on weight.

1. Raw materials and additives

The ethylene-methacrylic acid copolymers ("Copolymers") used in the examples are described in Table I. The ammonia used in the experiments was a 29% aqueous solution made by Kanto Kagaku K.K.

30

Table I

Composition		FR (dg/min)
Copolymer 1:	Ethylene/methacrylic acid (80 wt%/20 wt%)	60
Copolymer 2:	Ethylene/methacrylic acid (80 wt%/20 wt%)	300
Copolymer 3:	Ethylene/methacrylic acid (80 wt%/20 wt%)	500

2. Methods for evaluating the properties

Properties of the dispersions set forth in Table III were determined as follows:

- 5 1. Appearance: The measurement of Appearance of the resulting
dispersions was by visual examination. The
Appearance was considered to be
- a. "Uniform" if the dispersion contained no non-dispersed substances
and remained stable for an extended period of time;
- 10 b. "Non-uniform" if the dispersion contained non-dispersed substances or
precipitates; and
- c. "Not dispersed" if the substances did not disperse or remain dispersed
in the aqueous media.
- 15 2. pH: Based on JIS K6833. Obtained by measurement of a
sample using a commercial pH meter Horiba Custany
LAB "F12" pH meter.
3. Viscosity: Based on JIS K6833. Obtained by measurement using
a single-cylinder rotary viscometer Synchro Lectric
Viscometer.
- 20 4. Average Particle size: Measured by laser beam scattering-type particle
size distribution measuring apparatus NICOMP
370HPL.

APPLICATION EXAMPLES 1-3

25 Copolymers, ammonia, and distilled water were introduced into an
autoclave (300 mL) in the amounts shown in Table II, followed by stirring at
150°C for 60 minutes. The weight percent solid component in the aqueous
mixture in each case was 25 wt%. Evaluation results for dispersion properties are
shown in Table III.

COMPARATIVE EXAMPLES 1-4

30 Ammonia was used in the amounts shown in Table II in the same
process used in Application Examples 1-3. Evaluation results for the dispersion
property are shown in Table III.

5

Table II

Composition		
	Resin	Neutralization degree (NH ₃) (%)
Application Example 1	Copolymer 1	130
Application Example 2	Copolymer 2	130
Application Example 3	Copolymer 3	130
Comparative Example 1	Copolymer 1	100
Comparative Example 2	Copolymer 2	100
Comparative Example 3	Copolymer 3	100
Comparative Example 4	Copolymer 1	75
Comparative Example 5	Copolymer 3	75

Table III

	Appearance	pH	Viscosity	Average particle size
Application Example 1	Uniform	11.1	225	53
Application Example 2	Uniform	11.1	400	22
Application Example 3	Uniform	11.0	705	24
Comparative Example 1	Not dispersed			
Comparative Example 2	Non-uniform	10.9	370	26
Comparative Example 3	Non-uniform	11.0	555	29
Comparative Example 4	Not dispersed			
Comparative Example 5	Not dispersed			

5 **WHAT IS CLAIMED IS:**

1. A stable, uniform aqueous dispersion consisting essentially of a dispersion in water of component (A), an ethylene-methacrylic acid copolymer containing 15-35 wt% methacrylic acid, and component (B), ammonia in an amount required for neutralizing 110-150% of the carboxyl groups of component
10 (A).
2. The aqueous dispersion of claim 1 wherein the ethylene-methacrylic acid contains 18-30 wt% methacrylic acid.
- 15 3. The aqueous dispersion of claim 1 wherein the ethylene-methacrylic acid contains 15-25 wt% methacrylic acid.
2. The aqueous dispersion of claims 1, 2, or 3 wherein the ammonia is present in an amount sufficient to neutralize 120-140% of the carboxyl groups.
20 4.
5. The aqueous dispersion of claim 1 wherein the ethylene-methacrylic acid copolymer comprises 5-50 wt% of the dispersion and preferably has a melt flow rate of 50-2000 grams/10 minutes at 190°C/2160 gram load.
- 25 6. The aqueous dispersion of claim 3 wherein the ethylene-methacrylic acid copolymer comprises 5-50 wt% of the dispersion and preferably has a melt flow rate of 50-2000 grams/10 minutes at 190°C/2160 gram load.
- 30 7. The aqueous dispersion of claim 4 wherein the ethylene-methacrylic acid copolymer has a melt flow rate of 60-1500 grams/10 minutes at 190°C/2160 gram load.
- 35 8. The aqueous dispersion of claim 5 wherein the ethylene-methacrylic acid copolymer has a melt flow rate of 60-1500 grams/10 minutes at 190°C/2160 gram load.
9. A coated substrate obtained by applying the aqueous dispersion of claim 1, 2 or 3 to the substrate for coating, then drying to form a coated substrate.
- 40 10. The coated substrate wherein the substrate is a film.

5 11. A process for making a stable, uniform aqueous dispersion of ethylene-
methacrylic acid consisting essentially of mixing an ethylene-methacrylic acid
copolymer containing 15-35 wt% methacrylic acid in water in the presence of
sufficient ammonia to neutralize 110 to 150% of the carboxylic acid groups in the
10 ethylene-methacrylic acid copolymer for a sufficient time to uniformly disperse
the ethylene-methacrylic acid copolymer in the water.

12. The process of claim 11 wherein the mixing is carried out at a temperature
of about 90 to about 150°C for about 10 minutes to about 2 hours.

INTERNATIONAL SEARCH REPORT

Intel onal Application No

PCT/US 00/04754

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F8/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 269 822 A (OXY-WAX LTD.) 23 February 1994 (1994-02-23) page 2, paragraph 1 - paragraph 3 page 3, paragraph 6 - paragraph 7 page 4, paragraph 3 - paragraph 6; claims 1-5	1-12
X	GB 1 559 048 A (ASAHI-DOW LTD.) 16 January 1980 (1980-01-16) page 2, line 55 - line 108 page 3, line 20 - line 114; claims 1-18 ----- -/--	1-12

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

28 June 2000

Date of mailing of the international search report

11/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Permentier, W

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/04754

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9832 Derwent Publications Ltd., London, GB; Class A14, AN 1998-371144 XP002141301 & JP 10 147683 A (MITSUI DU PONT POLYCHEMICAL KK), 2 June 1998 (1998-06-02) abstract</p> <p>----</p>	1-12
X	<p>CH 476 041 A (BAYER AG) 31 July 1969 (1969-07-31) column 3, line 26 - line 47; claim 1</p> <p>----</p>	1-12
X	<p>BE 657 147 A (UCC) 1 April 1965 (1965-04-01) page 3, paragraph 3 page 7, paragraph 4 -page 8, paragraph 1 page 8, paragraph 4 -page 9, paragraph 1 page 11 -page 12</p> <p>----</p>	1-12
A	<p>US 3 674 896 A (C. L. PURCELL) 4 July 1972 (1972-07-04) column 1, line 31 -column 2, line 14 column 3, line 1 - line 3 column 3, line 49 - line 75 column 4, line 32 - line 75; claims 1-10</p> <p>----</p>	1
A	<p>US 5 430 111 A (F. P. RECCHIA) 4 July 1995 (1995-07-04) column 5, line 52 -column 7, line 52; claims 1-13</p> <p>----</p>	1
A	<p>WO 92 13012 A (THE DOW CHEMICAL COMPANY) 6 August 1992 (1992-08-06) page 4, line 1 - line 21 page 5, line 5 - line 31 page 6, line 3 -page 7, line 7 page 8, line 29 -page 9, line 2; claims 1-13</p> <p>----</p>	1
A	<p>EP 0 523 993 A (CARGILL, INC.) 20 January 1993 (1993-01-20) page 3, line 45 - line 54; claims 1-15</p> <p>----</p>	1
A	<p>EP 0 842 954 A (BASF AG) 20 May 1998 (1998-05-20) page 4, line 2 - line 15; claims 1-12</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 00/04754

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 2269822	A	23-02-1994	NONE		
GB 1559048	A	16-01-1980	NONE		
JP 10147683	A	02-06-1998	NONE		
CH 476041	A	31-07-1969	BE	695197 A	14-08-1967
			DE	1595601 A	30-04-1970
			FR	1514524 A	15-05-1968
			GB	1123285 A	
			NL	6702067 A	11-09-1967
BE 657147	A	01-04-1965	DE	1519415 A	21-05-1970
			FR	1419138 A	16-02-1966
			GB	1096946 A	
			NL	6414740 A	21-06-1965
			SE	342825 B	21-02-1972
US 3674896	A	04-07-1972	AT	296459 B	15-01-1972
			AU	447937 B	17-04-1974
			AU	4976069 A	19-11-1970
			BE	702016 A	29-01-1968
			CH	208368 A	15-11-1971
			CH	485827 B	15-02-1970
			CH	520226 B	15-03-1972
			DE	1646160 A	08-07-1971
			FI	53334 B	30-12-1977
			FR	1532958 A	28-11-1968
			GB	1201811 A	12-08-1970
			NL	6710476 A	29-01-1968
US 5430111	A	04-07-1995	US	5591806 A	07-01-1997
WO 9213012	A	06-08-1992	US	5206279 A	27-04-1993
			AU	651874 B	04-08-1994
			AU	1333192 A	27-08-1992
			CA	2077667 A	26-07-1992
			EP	0522146 A	13-01-1993
			FI	924254 A	23-09-1992
			US	5387635 A	07-02-1995
EP 523993	A	20-01-1993	US	5319019 A	07-06-1994
			EP	0523992 A	20-01-1993
			EP	0523994 A	20-01-1993
			JP	5247309 A	24-09-1993
			JP	5247310 A	24-09-1993
			JP	5239302 A	17-09-1993
			JP	5239303 A	17-09-1993
			US	5380771 A	10-01-1995
			US	5356988 A	18-10-1994
EP 842954	A	20-05-1998	DE	19647564 A	20-05-1998
			US	5880233 A	09-03-1999